into the broad range previously recorded (2.18–2.718 Å),[5] but there are so few examples that a "normal" distance is yet to be defined. The average Al–S distance in the most closely related structure, that of $(\mathrm{Me_2Al}\text{-}\mu\text{-}\mathrm{SMe})_n$, is 2.348 Å in the solid state[6] and 2.370 Å for the dimeric molecule in the gas phase[7] are very close to the values obtained in 1. All of the bond angles in 1 are reasonable for organoaluminum complexes. The one significant feature other than the head-to-head arrangement of the bridging ligands is that the two methyl groups on a given Al atom may be equivalent but differ from those on the other Al center. On the basis of this fact one would anticipate that the ^{1}H NMR spectrum should show two lines for the methyl groups bound to the aluminum.

Examination of the ^{1}H NMR spectra of a sample of 1 in toluene-d_8 shows a broadened resonance line for the methyl groups at room temperature which indicates that some form of exchange process is occurring. A variable-temperature NMR study shown in Figure 2 shows more complex behavior. At high temperature a single sharp line is observed for the Al methyl groups. This broadens and separates into two lines of unequal intensity as the temperature is lowered. A further decrease in temperature leads to a change in the intensity of these lines so that they become of equal intensity within experimental error at approximately −50 °C.

Examination of the ^{1}H NMR spectra of 2 as a function of temperature shows similar results to a first approximation. Closer examination of the low-temperature spectrum shows an additional feature that bears directly on the structure of the compounds in solution. At low temperature the methylene protons of the ethyl groups become diastereotopic as seen in Figure 3. This implies the induction of prochirality at the aluminum center and is identical with the behavior found in $[\mathrm{R_2Al(O\text{-}(\mathit{R})\text{-}CHC_6H_5((\mathit{S})\text{-}CH((\mathit{S})\text{-}NHCH_3)CH_3)}]_2$ which has been shown to have a five-coordinate Al center.[8] Formation of a symmetrical five-coordinate aluminum atoms, however, would make all four ethyl groups identical contrary to their observed behavior. Close examination of the head-to-head structure observed for 1 shows that the ethyl groups in 2 for a molecule of similar structure would be diastereotopic and would account for the observed spectrum.

The conclusions at present are that the pyridine-2-thiol reacts with alkylaluminum derivatives to give new dialkylaluminum thiolates which form head-to-head dimers on crystallization. In solution these dimers undergo rapid rearrangements on the NMR scale near room temperature and above. As the temperature is lowered to intermediate values, there are at least two environments, but of unequal population. This is consistent with formation of two or more species that are undergoing slow exchange. Possible structures include head-to-tail coordination, simple sulfur-bridged derivatives, or more complex species which may involve five- or six-coordinate aluminum centers. At low temperature (<−35 °C) the equilibrium has shifted to two equivalent lines for the methyl groups that can be easily accounted for in terms of the observed solid-state structure. This explanation also accounts for the behavior of the 2, including the observation of diastereotopic methylene protons. Further studies are now in progress to explore the unusual structural properties of aluminum-thiolates and their behavior in solution.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. V.S.J.d.M. acknowledges a Rumble fellowship provided by Wayne State University for support of his graduate studies. We also thank Professor B. Edwards and the Department of Biochemisty, Wayne State University Medical School for use of the X-ray diffractometer.

Supplementary Material Available: Tables of torsion angles, least-squares planes, anisotropic thermal parameters, hydrogen atom positional coordinates, and isotropic thermal parameters (12 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Silyl-Substituted Diphosphenes. Synthesis, Structure, and Modes of Decomposition

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Summary: The first stable silyl-substituted diphosphenes $(2,4,6\text{-}t\text{-}\mathrm{Bu_3C_6H_2})\mathrm{P{=}PSiPh_3}$ (**1**) and $\mathrm{(Me_3Si)_3CP{=}PSiPh_3}$ (**2**) have been synthesized. The structure of **2** has been determined by X-ray crystallography. Compound **1** undergoes slow head-to-head dimerization. The less stable diphosphene $\mathrm{(Me_3Si)_3CP{=}PSiMe_3}$ (**7**) has also been prepared. Compound **7** decomposes to a bicyclobutane-analogous tetraphosphane.

Silyl-substituted diphosphenes of the type $\mathrm{RP{=}PSiR'_3}$ are of potential importance as $\mathrm{RP{=}P}$ unit transfer reagents. A compound of composition $\mathrm{ArP{=}PSiMe_3}$ (Ar = $2,4,6\text{-}t\text{-}\mathrm{Bu_3C_6H_2}$) has, in fact, been implied from spectroscopic data;[1] however, so far no silyl-substituted diphosphene has been isolated. We report the syntheses of the first kinetically stabilized silyl-substituted diphosphenes $\mathrm{ArP{=}PSiPh_3}$ (1) and $\mathrm{(Me_3Si)_3CP{=}PSiPh_3}$ (2) along with an X-ray analysis of 2.

The new lithium phosphide $\mathrm{LiP(SiMe_3)(SiPh_3)}$ (3) was prepared by the following sequence of reactions.[2]

$$\mathrm{NaAl(PH_2)_4} \xrightarrow{\mathrm{Ph_3SiCl}} \mathrm{Ph_3SiPH_2} \xrightarrow{\mathrm{MeLi}} \mathrm{Ph_3SiP(H)Li} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{Ph_3Si(Me_3Si)PH} \xrightarrow{\mathrm{MeLi}} \underset{\mathbf{3}}{\mathrm{Ph_3Si(Me_3Si)PLi}}$$

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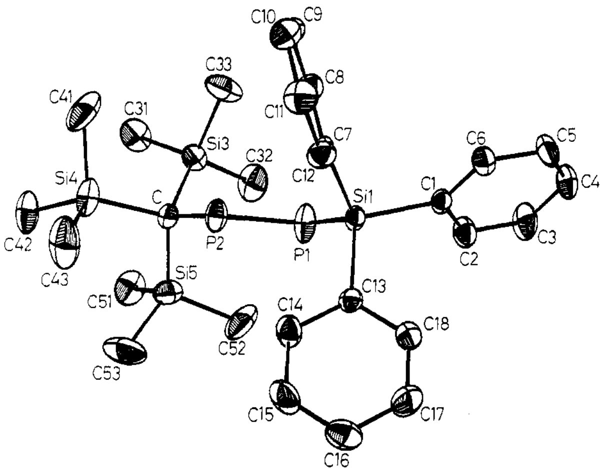
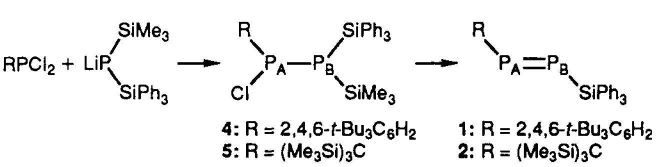


Figure 1. Structure of 2 in the crystal showing the atom numbering scheme. Selected bond lengths (Å) and bond angles (deg): P1–P2 = 2.005 (2), P1–Si1 = 2.269 (2), P2–C = 1.868 (6); P2–P1–Si1 = 98.65 (8), P1–P2–C = 110.5 (1), Si1–P1–P2–C torsion angle = 0.21°.

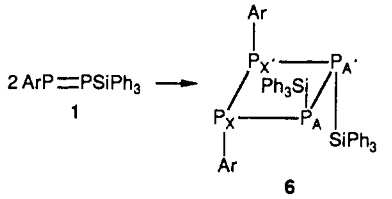
Treatment of 3 with equimolar quantities of $RPCl_2$ (R = 2,4,6-*t*-$Bu_3C_6H_2$, $(Me_3Si)_3C$) in Et_2O solution afforded 1 and 2 in virtually quantitative yields.[4] In both cases, the



intermediate diphosphanes 4 and 5 were detected by $^{31}P\{^1H\}$ NMR spectroscopy.[5] Compounds 1 and 2 were characterized by mass spectroscopy[5] and also by the appearance of an AB pattern in the $^{31}P\{^1H\}$ spectra in a region characteristic of the P=P chromophore.[6]

Interestingly, crystals of 2 are rose-pink while 1, like other diphosphenes, exhibits an orange color. An X-ray crystal structure of 2 was therefore considered desirable.[7] Individual molecules of 2 adopt a trans geometry and the P=P bond length of 2.005 (2) Å is consistent with a bond order of 2. The P–P–Si angle of 98.65 (8)° is the smallest P–P–X angle reported for a diphosphene.[6] Moreover, the P–P–C angle of 110.5 (1)° in 2 is ~2° larger than that in $(Me_3Si)_3CP{=}PC(SiMe_3)_3$.[8] Since this trend is inconsistent with steric demands we attribute it to electronic effects of the Ph_3Si group. The P(2)···Si(1) distance of 3.246 Å indicates that there is no bonding interaction between these atoms. The P(1)–Si(1) distance [2.269 (2) Å] falls in the normal range for a single bond.

Compound 2 is stable for extended periods both in solution and in the solid phase. However, NMR experiments indicate that in THF solution at ambient temperature, 1 undergoes head-to-head dimerization over a 2-day period.



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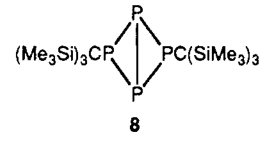
The use of molecular models reveals that the all-trans isomer 6 results from the minimization of steric effects. Diphosphene dimerization of this type has been postulated previously but not observed.[9]

In order to explore the decomposition mode of an R_3Si-substituted diphosphene, $(Me_3Si)_3CP{=}PSiMe_3$ (7), was prepared by treatment of $LiP(SiMe_3)_2$[10] with $(Me_3Si)_3CPCl_2$ in Et_2O solution using an analogous procedure to that described for the synthesis of 1 and 2.[4] Compound 7 is unstable at room temperature; hence identification is based on $^{31}P\{^1H\}$ NMR spectroscopic data.[5] Upon standing for 5 days at −20 °C, Et_2O solutions of 7 decompose to the bicyclobutane-analogous tetraphosphane 8.[11] No evidence was found for a cyclotetraphosphane



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akin to 6. It appears that the dimerization of 7 is precluded by the steric demands of the $(Me_3Si)_3C$ groups.

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation

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(2) (Triphenylsilyl)phosphine was prepared via the reaction of $NaAl(PH_2)_4$ with Ph_3SiCl according to the literature procedure.[3] Methyllithium (3.2 mL of 1.56 M solution in hexane) was added slowly to a solution of 1.56 g (5.0 mmol) of Ph_3SiPH_2 in 25 mL of THF at −78 °C. Following the addition, the stirred reaction mixture was allowed to warm to room temperature. After 1 h, the THF and hexane were pumped off in vacuo and replaced by 50 mL of Et_2O. The resulting solution of $Ph_3SiP(H)Li$ was then added to an excess of Me_3SiCl (2.2 g, 20.0 mmol) in 40 mL of Et_2O at −78 °C. The reaction mixture was stirred for 1 h after reaching room temperature, following which the precipitated LiCl was removed by filtration. The Et_2O was stripped from the filtrate leaving liquid $Ph_3Si(Me_3Si)PH$. The $Ph_3Si(Me_3Si)PH$ was then dissolved in 20 mL of THF, cooled to −78 °C, and treated with MeLi (3.2 mL of 1.56 M solution in hexane). The resulting solution of $Ph_3Si(Me_3Si)PLi$ (3) was stirred for 1 h after reaching room temperature. Finally the THF and hexane were stripped off and replaced by 20 mL of Et_2O. ^{31}P NMR (121.5 MHz, 295 K, 85% H_3PO_4 external standard): Ph_3SiPH_2 (hexane), $\delta = -247.9$, $^1J_{PH} = 182.8$ Hz; $Ph_3SiP(H)Li(THF)$, $\delta = -306.1$, $^1J_{PH} = 152.6$ Hz; $Ph_3Si(Me_3Si)PH$ (CH_2Cl_2), $\delta = -244.9$, $^1J_{PH} = 189.7$, $^3J_{PH} = 4.6$ Hz; $Ph_3Si(Me_3Si)PLi$ (Et_2O), $\delta = -313.1$.

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(4) Preparation of 1 and 2: 5.0 mmol of $RPCl_2$ (R = 2,4,6-*t*-$Bu_3C_6H_2$, 1.74 g; R = $(Me_3Si)_3C$, 1.67 g) was dissolved in 20 mL of Et_2O. After these solutions were cooled to −78 °C, 1.85 g (5.0 mmol) of $Ph_3Si(Me_3Si)PLi$[2] in 20 mL of Et_2O was added dropwise. The reaction mixtures were allowed to warm to room temperature and then filtered to remove the precipitated LiCl. $^{31}P\{^1H\}$ NMR assays[5] of the resulting solutions revealed the exclusive presence of 4 and 5. Conversion to 1 and 2 was effected by overnight stirring at ambient temperature. The isolated yields of 1 and 2 were 74% and 61%, respectively, after recrystallization from hexane.

(5) ^{31}P NMR (121.5 MHz, 295 K, 85% H_3PO_4 external standard): 1 (THF), $\delta_A = 457.7$, $\delta_B = 641.9$, $^1J_{PP} = 588.7$ Hz; 2 (Et_2O), $\delta_A = 511.8$, $\delta_B = 711.4$, $^1J_{PP} = 633.1$ Hz. 3 (Et_2O), $\delta = 313.1$; 4 (Et_2O) isomer 1, $\delta_A = 97.3$, $\delta_B = -147.4$, $^1J_{PP} = 211.0$ Hz; 4 (Et_2O) isomer 2, $\delta_A = 96.9$, $\delta_B = -144.0$, $^1J_{PP} = 251.1$ Hz; 5 (Et_2O), $\delta_A = 155.3$, $\delta_B = -144.0$, $^1J_{PP} = 450.7$ Hz; 6 (THF, AA′XX′), $\delta_A = -134.6$, $\delta_B = 18.8$, $J_{AA'} = 175.6$, $J_{XX'} = 92.8$, $J_{AX} = 117.8$, $J_{AX'} = -60.7$ Hz; 7 (Et_2O), $\delta_A = 544.1$, $\delta_B = 686.9$, $^1J_{PP} = 633.2$ Hz; 8 (Et_2O, A_2X_2), $\delta_A = -333.9$, $\delta_B = -111.2$, $^1J_{AX} = 203.2$ Hz. MS (*m*/*z*): 1, 567 ($M^+ + H$, 100%, CI), 2, 552 (M^+, 100%, EI).

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(7) 2: triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$; $a = 9.312$ (4), $b = 22.436$ (11), $c = 8.857$ (2) Å; $\alpha = 100.98$ (3), $\beta = 115.31$ (3), $\gamma = 88.95$ (4)°; $V = 1638$ Å^3; d(calcd) = 1.121 g cm^{-3}; $3° < 2\theta < 55°$ (Mo Kα, $\lambda = 0.71069$ Å; $\mu = 2.9$ cm^{-1}). A total of 7500 unique reflections collected at 23 °C, of which 4205 [$I > 3.0\sigma(I)$] were used to solve (direct methods) and refine (full-matrix least squares) the structure. Hydrogen atoms H(8) through H(18) were refined in calculated positions. The final R and R_w values were 0.072 and 0.080, respectively.

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(10) Fritz, G.; Hölderich, W. *Z. Anorg. Allg. Chem.* **1976**, *422*, 104.

(11) A similar reaction takes place upon UV irradiation of (Me_5C_5)-$P{=}P(C_5Me_5)$. See: Jutzi, P.; Meyer, U. *J. Organomet. Chem.* **1987**, *333*, C18.

for generous financial support. P.C.K. thanks the Deutsche Forschungsgemeinschaft for a fellowship.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters (11 pages); a listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

Pyrrolyl–Transition Metal–Carboranyl Double-Decker and Triple-Decker Sandwich Complexes[1]

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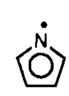
Received May 30, 1989

Summary: A series of pyrrolyl–transition metal sandwich complexes stabilized by cyclic $Et_2C_2B_3H_n^{n-7}$ (n = 3, 5) carborane ligands, including the first pyrrolyl triple-decker compounds, has been prepared. Reaction of the *nido*-$Et_2C_2B_4H_5^-$ ion with $CoCl_2$ and dimethyl- or tetramethylpyrrolide ions in THF followed by TMEDA (tetramethylethylenediamine) generated (η^5-$NC_4Me_2R_2$)Co($Et_2C_2B_3H_5$) (R = Me, H) sandwich complexes, which in turn were converted into a bis(pyrrolyl) triple decker (η^5-NC_4Me_4)$_2$$Co_2$($\mu$,$\eta^5$-$Et_2C_2B_3H_3$), dicobalt triple deckers (η^5-$NC_4Me_2R_2$)Co(μ,η^5-$Et_2C_2B_3H_3$)Co(η^5-C_5Me_5), and cobalt-ruthenium triple deckers (η^5-$NC_4Me_2R_2$)Co(μ,η^5-$Et_2C_2B_3H_3$)Ru(η^6-1,4-$MeC_6H_4CHMe_2$), all obtained as air-stable crystalline solids.

The transition-metal chemistry of nitrogen heterocycles is dominated by σ-interactions between the metal and the electron lone pair on nitrogen.[2] Accordingly, there are relatively few well-characterized examples of metal sandwich complexes incorporating η^5-bonded pyrrolyl (1) or pyrrole (2) ligands; most of those reported are "half-sandwich" species such as (η^5-pyrrole)$Cr(CO)_3$.[3] Thus, diazaferrocene [$(C_4H_4N)_2Fe$] is unknown, although its octa-*C*-methyl derivative has recently been prepared[4] as a bis(tetramethylpyrrolyl) adduct.



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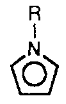

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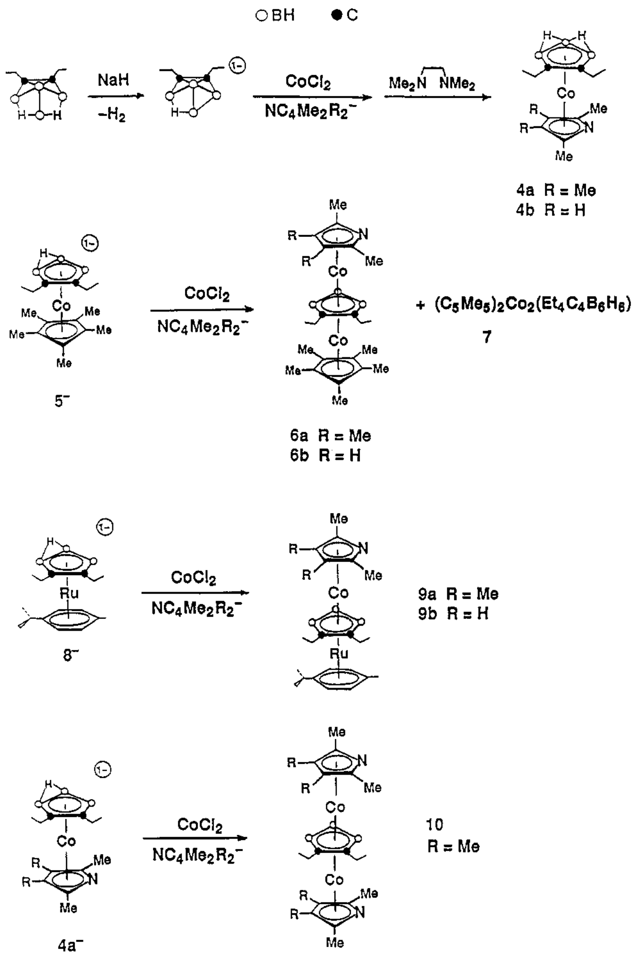
We report here the designed synthesis and characterization of novel carboranyl–metal–pyrrolyl complexes and their conversion to triple-decker sandwiches containing pyrrolyl ligands, the first reported examples of this genre. This chemistry exploits the remarkable ability of the small carborane ligands *nido*-$R_2C_2B_4H_4^{2-}$ and *cyclo*-$R_2C_2B_3H_3^{4-}$ to stabilize transition metal–organometallic systems that are otherwise unstable or nonexistent,[1b,5] e.g., the first neutral triple-decker complexes,[6] (η^5-C_5H_5)$_2$$Co_2$($\mu$,$\eta^5$-$R_2C_2B_3H_3$). The reaction of the $Et_2C_2B_4H_5^-$ ion with $CoCl_2$ and the 2,3,4,5-tetramethylpyrrolide or 2,5-dimethylpyrrolide ion in THF gave a mixture of *closo*-(η^5-$NC_4Me_2R_2$)Co($Et_2C_2B_4H_4$) (3) and *nido*-(η^5-$NC_4Me_2R_2$)-Co($Et_2C_2B_3H_5$) (4) as shown by NMR and mass spectra. The addition of wet tetramethylethylenediamine (TMEDA) to the mixture converted all of the **3** to **4** via "decapitation" (apex BH removal), affording the desired **4a** or **4b** in 35–45% yields (Scheme I).[7]

Scheme I



Deprotonation of the known *nido*-cobaltacarborane[1b] (C_5Me_5)Co($Et_2C_2B_3H_5$) (**5**) and the subsequent reaction of

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[1] (a) Organotransition-Metal Metallacarboranes. 14. (b) Parts 12 and 13: Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776, 4784.

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[3] Öfele, K.; Dotzauer, E. *J. Organomet. Chem.* **1971**, *30*, 211.

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[7] **4a**: anhydrous $CoCl_2$ (0.170 g, 1.32 mmol) in 50 mL of THF was combined with $LiNC_4Me_4$ (prepared from HNC_4Me_4 (1.80 g, 1.46 mmol) and *n*-C_4H_9Li in 30 mL of THF) and stirred for 1 h. $Na^+(Et_2C_2B_4H_5)^-$ (1.16 mmol, prepared from 0.153 g of $Et_2C_2B_4H_6$) and NaH in 50 mL of THF, was added, the mixture was stirred for 1 h and opened to the atmosphere, and the THF was removed by rotary evaporation. The residue was extracted with diethyl ether, the extract was filtered through 2 cm of silica gel and concentration by rotary evaporation, and 10 mL of TMEDA and 0.5 mL of water were added and the solution stirred for 15 min. Following the removal of volatiles by evaporation, the residue was extracted in *n*-hexane and filtered through silica gel, after which the silica was washed with diethyl ether and the filtrate rotary-evaporated to give **4a** as a yellow oil (0.123 g, 35%): ^1H NMR (δ, ppm, $CDCl_3$) −5.95 (s, 2 H, bridge H), 1.13 (t, 6 H, ethyl CH_3), 1.88 (s, 6 H, 2,5-CH_3), 2.02 (s, 6 H, 3,4-CH_3), 2.07 (m, 2 H, ethyl CH_2), 2.18 (m, 2 H, ethyl CH_2); ^{11}B NMR (^1H-decoupled, δ, ppm relative to BF_3 etherate, CH_2Cl_2) 6.12 (1 B, B[5]), 3.44 (2 B, B[4,6]); IR (neat, cm^{-1}[2962 s, 2918 s, 2862 s, 2525 s, 2360 w, 2329 w, 1862 m, 1725 w, 1612 m, 1547 m, 1450 s, 1374 s, 1330 m, 1275 m, 1110 m, 1022 m, 921 m; MS (70 eV) *m/z* 301 (base peak), parent, 181, loss of pyrrolyl; exact mass calcd for $^{59}Co^{14}N^{12}C_{14}{}^{11}B_3{}^1H_{27}{}^+$ 301.1755, found 301.1753. A procedure analogous to that employed for **4a** but employing the 2,5-dimethylpyrrolide ion gave **4b** as a yellow oil (0.209 g, 44%).

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